

Title:

**O/M Ratio Measurement in Pure and Mixed Oxide
Fuels - Where are We Now ?**

Author(s):

J. Rubin, K. Chidester and M. Thompson

Submitted to:

<http://lib-www.lanl.gov/la-pubs/00357110.pdf>

O/M Ratio Measurement in Pure and Mixed Oxide Fuels – Where are We Now ?

J. Rubin^{*}, K. Chidester¹ and M. Thompson¹

Los Alamos National Laboratory

^{*}Mail Stop E-574, ¹ Mail Stop E530, Los Alamos, New Mexico 87545

phone : (505) 667-3294

fax : (505) 665-7815

^{*}e-mail: jbr@lanl.gov

KEYWORDS: Chemistry, Methods, Fuel

ABSTRACT

The oxygen-to-metal (O/M) ratio is one of the most critical parameters of nuclear fuel fabrication, and its measurement is closely monitored for manufacturing process control and to ensure the service behavior of the final product. Thermogravimetry is the most widely used method, the procedure for which has remained largely unchanged since its development some thirty years ago. It was not clear to us, however, that this method is still the optimum one in light of advances in instrumentation, and in the current regulatory environment, particularly with regard to waste management and disposal.

As part of the MOX fuel fabrication program at Los Alamos, we conducted a comprehensive review of methods for O/M measurements in UO₂, PuO₂ and mixed oxide fuels for thermal reactors. A concerted effort was made to access information not available in the open literature. We identified approximately thirty five

experimental methods that (a) have been developed with the intent of measuring O/M, (b) provided O/M indirectly by suitable reduction of the measured data, or (c) *could* provide O/M data with suitable data reduction or when combined with other methods. We will discuss the relative strengths and weaknesses of these methods in their application to current routine and small-lot production environment.

INTRODUCTION

The scale-down in the US and Russian nuclear weapons stockpiles has produced a surplus of weapons grade plutonium and highly enriched uranium. According to a recent National Academy of Sciences Report "Some 10,000-20,000 warheads in the United States and at least a similar number in the former Soviet Union are likely to fall into this {excess} category, depending on the ultimate scope of reductions and decisions concerning the size of non-deployed reserves. These excess nuclear weapons on the two sides could contain well over 100

metric tons of plutonium, and perhaps 1,000 metric tons of HEU, much of which may also be declared excess to military needs.”[1] This excess weapons Pu is considered to be a threat for potential proliferation and various disposal options have been examined. The currently favored disposition routes for surplus weapons-grade Pu are (1) incorporation into mixed-oxide fuel (MOX), and “burning” in civilian nuclear reactors, and (2) immobilization of the Pu together with intensely radioactive fission products in glass.

The use of MOX as a nuclear reactor fuel is well established, particularly in Europe and Japan. There are, however, no MOX fuel fabrication facilities in the US, owing to the fact that there are no domestic electricity generators using MOX fuel. (This appears to be primarily a public relations issue, as opposed to a technical issue.) Consequently, there is little current domestic expertise in analytical measurements as specifically applicable to MOX fuels.

The primary purpose of this investigation, then, was to evaluate existing analytical techniques for their applicability to O/M measurements of MOX derived from excess weapons plutonium. The composition of MOX pellets, derived from this PuO_2 feedstock, presents a somewhat different situation, in terms of pellet fabrication and certification, than is the case for PuO_2 derived from pure Pu metal. The second objective of this investigation was to bring up-to-date the literature on O/M measurement methods, which has not been undertaken in over twenty years. Previous reviews were presented by Lyon in 1963,[2] Perron in 1968,[3] Florence in 1972,[4] and most recently by Swanson in 1975.[5]

The techniques known to have been applied to O/M measurement have been evaluated, as well as a large number of experimental studies of various thermal, physical, and mechanical properties, which, although never directly applied to O/M determination, have been studied in sufficient detail such that an experimental database exists which might be useful for the development of an analytical method.

There are several classification schemes that can be used to organize O/M measurement methods. The most popular schemes are based on (a) whether the analysis is performed in solution (wet chemical) or on solid material (dry), and (b) whether the concentration of major constituents are analyzed directly (direct) or are inferred (indirect). Figures 1 and 2 give our classification, which is based rather loosely on whether or not the analysis method requires a change in the physical state of the sample. The methods listed in Figures 1 and 2 were those that were deemed applicable to the O/M measurement problem, as per the requirement of previous application or existence of a suitable database based on that method. Table 1 gives some baseline values for precision and accuracy of these methods.

The ideal analytical method for O/M determination would have the following attributes:

1. High accuracy and precision over all ranges of mixed oxide stoichiometry, and therefore of mixed oxide compositions,
2. Non-destructive to the pellet,
3. Rapid, so that sample throughput is high (The ability to measure multiple samples simultaneously would be optimal),

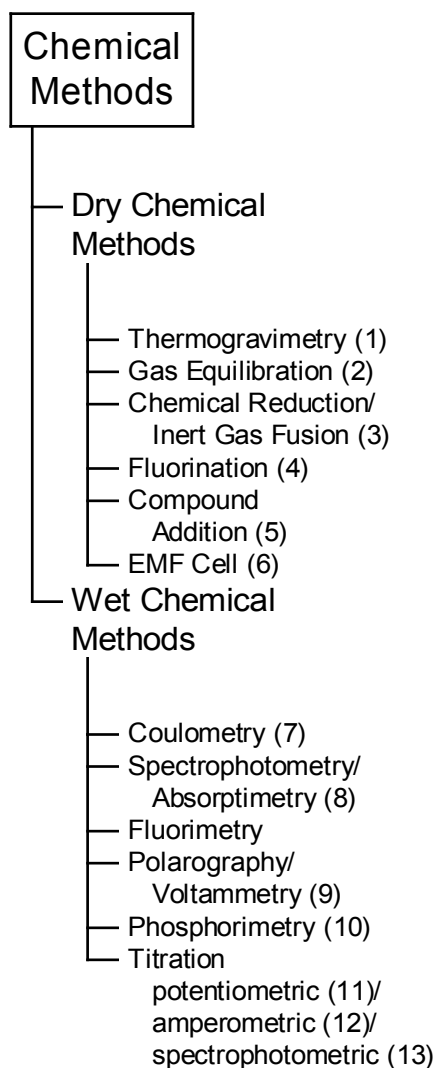


Figure 1. Methods applied to the measurement of O/M ratio in pure and mixed oxide fuels.

4. Capable of being at least partially automated, to eliminate as many measurement errors as possible,
5. Inexpensive to implement and operate,
6. Small "footprint"
7. Does not generate hazardous and/or radioactive wastes
8. Capable of direct measurement, so that the establishment of calibration functions and method bias are unnecessary.
9. Uses instrumentation/equipment that is commercially available.

While a routine (in-plant) analytical

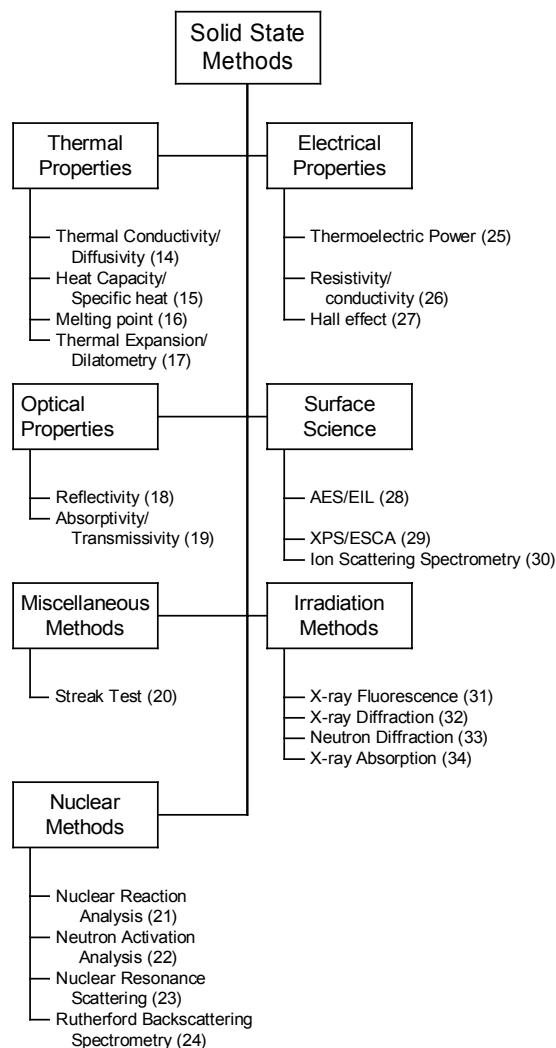


Figure 2. Methods applied to the measurement of O/M ratio in pure and mixed oxide fuels.

method will possess as many of these attributes as possible, they must be weighed against analysis time, complexity, cost, availability of equipment, etc.

Owing to the differences in atomic number, mass chemical behavior, reactivity and physical properties of oxygen versus (U and Pu), it is difficult for one method to simultaneously provide high-precision data on both elements, and thereby give an accurate O/M ratio. The logical alternative is to determine O/M ratios by measuring the oxygen and metal

contents *independently but simultaneously*. There have been two reported approaches: (1) measurement of oxygen by inert gas fusion and total metals (U + Pu) content by controlled-potential coulometry. A precision of ± 0.005 in O/M for 1 g samples was claimed,[6,7] and (2) measurement of oxygen content by lattice parameter measurement by x-ray diffraction and (Pu/U) ratio by x-ray fluorescence.[8] While such combined methods achieved some level of success, they were viewed as extremely time-consuming and labor intensive, while requiring dedicated analytical chemistry facilities. They were therefore not seen as suitable for routine analytical use. Consequently, it became industry-wide practice to use an indirect method.

It appears that most fuel fabricators use the indirect method of thermogravimetry for routine O/M analysis. Among the various thermal treatments associated with the thermogravimetric method, there are a few that have become 'standard techniques'. These include the thermal treatments proposed by Lyon and McNeilly and Chikalla (the latter is essentially the ASTM-standard method). This analysis method, as with all of the indirect analytical methods, suffers from the fact that there are no (O/M) standards.[9,10,11] In the absence of such standards, thermodynamics has quite often been used. For example, the thermogravimetric method relies on the establishment of an oxygen potential with which a stoichiometric oxide is in equilibrium. The attractiveness of this approach is that regardless of the thermal treatment conditions used to establish the required oxygen potential (furnace gas composition, temperature, etc.), the same, final

oxide composition should result. In practice, however, there are questions about the equivalency of different treatment schedules. A round-robin study, involving seven different laboratories, was conducted to establish the bias and precision of the thermogravimetric method.[12] Each laboratory was to analyze a batch of hypostoichiometric mixed oxide pellets for (O/M). A specific thermal treatment was to be used. It turns out that several different thermal methods were actually used, with each laboratory using its preferred treatment schedule. If the assumption of method equivalency is correct, this variation in treatment process should not have affected the measured (O/M)'s (assuming that each method establishes the same oxygen potential). It turned out, however, that there were statistically significant differences in the measured (O/M)'s. In a subsequent study where the same thermal treatment method was used, the results of an inter-laboratory comparison study showed an acceptable variation of ± 0.003 in O/M.[13]

After evaluating the methods shown in Figures 1 and 2, it was recommended that one of two indirect methods, standardized by a direct method, be adopted for use. The two indirect methods are

1. Solid state coulometric titration to the MO_2 reference end-point, or
2. Thermogravimetry to the MO_2 reference end point.

Solid State Coulometric Titration

If two electronically conductive materials whose common chemical constituents are present in different chemical potentials are physically separated by a third material that possesses the unique property that it

can conduct an ion common to both of the aforementioned materials, a voltage difference can be measured. This is the basic principle behind a galvanic or electromotive force (EMF) cell. The chemical potential of oxygen for a given single-phase solid oxide has a unique temperature and stoichiometry dependent value. A measurement of the chemical potential of oxygen can provide important information on oxygen concentration within the metal oxide. One method for measuring the chemical potential of oxygen in a metal oxide is by making the metal oxide one electrode (the working electrode) of a solid-state EMF cell and by making the reference electrode out of a metal/metal oxide mixture where the chemical potential of oxygen is thermodynamically fixed by the Gibb's phase rule. The electric potential measured across this cell, at a given temperature, is then proportional to the difference in oxygen chemical potential between the metal oxide and by the oxygen chemical potential set, or fixed, by the reference electrode.

The overall cell reaction involves the removal of oxygen from the less electropositive side of the cell (uranium oxide or mixed oxide) and the addition of oxygen to the more

electropositive side of the cell (reference electrode). The voltage generated across the cell is a measure of the difference in oxygen potential between the two materials. Such a cell can be operated in either of two modes:

1. *Potentiostatic* The steady-state rest voltage between the working and reference electrodes is measured, in the absence of current flow. This method is analogous to an aqueous potentiostatic titration.
2. *Coulometric* A constant potential is applied between the working and reference electrodes, and the resulting current is measured. This mode of operation is analogous to an aqueous coulometric titration.

The desirable features of the potentiostatic and coulometric operations can be combined, as shown in Figure 3. Once the pellet has been heated, in an inert atmosphere, a potentiostatic measurement of the furnace atmosphere will give the oxygen potential from the Nernst equation. This static measurement reveals whether the pellet is hypo- or hyperstoichiometric. Then, an oxygen-containing carrier gas of known oxygen potential is admitted into the furnace. A coulometric titration to the

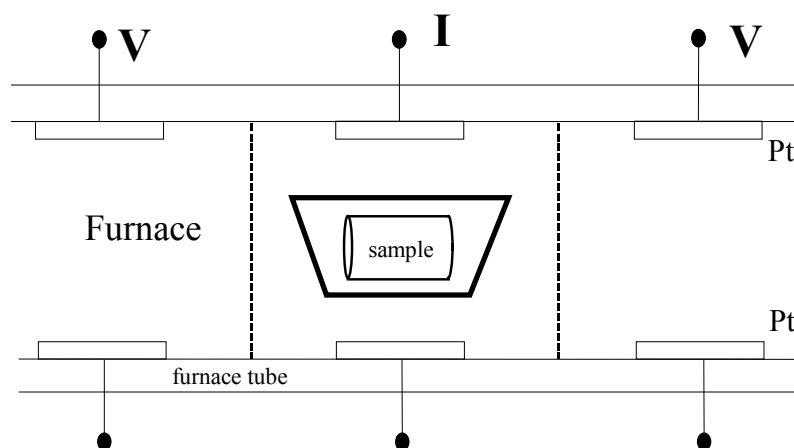


Figure 3. Schematic diagram of a combined EMF/coulometric titration apparatus.

stoichiometric end-point ($\text{MO}_{2.000}$) gives the deviation from stoichiometry. From the schematic, *it is not necessary for the working electrode to be in physical contact with the electrolyte*. In fact, systematic errors can be minimized by transferring the charge carriers using a carrier gas, in lieu of physical contact.[14] For example, instead of “pumping” oxygen out of the sample, thereby reducing it to pure metal, the experiment might involve reduction of hyperstoichiometric oxide to stoichiometric using a (inert gas/ H_2) gas stream

The advantages of solid-state coulometric titration are

1. The measurement of charge is an inherently more accurate process than is the measurement of potential, since the current reference for the titration method is the electron, whose value is known very accurately.
2. A calibration curve, based on EMF vs. O/M, which is required for the potentiostatic operation, is not needed for the coulometric operation. However, if the titration is carried out to a pre-determined reference state, this reference state must have been previously defined. (The same is true for the thermogravimetric method.)
3. An EMF cell, operated as a solid-state coulometric titration cell, would not be subject to problems associated with the use of reference electrode, such as depletion of the metal oxide.
4. When the deviation from stoichiometry becomes small ($x \rightarrow 0$), both EMF/Galvanic Cells and thermogravimetry lose precision. The former due to the very small potentials which must be measured, the latter due to systematic errors such as buoyancy effects and weighing errors. Solid-

state coulometric titration, however, retains high precision for small x .

The limitations of the titration method are

1. The metal content ($\text{U} + \text{Pu}$) must be accurately known, since only the oxygen activity is determined.
2. Unless an apparatus is built which allows the samples to be introduced into the measuring furnace at the measuring temperature, the speed of an analysis will be limited by the time to reach temperature, as well as time to establish equilibrium.

CONCLUSIONS

Solid state coulometric titration is currently used extensively in studies of phase equilibria, defect chemistry, thermochemical measurement of oxides, including ferrites.[15] Also, the apparatus required for this analysis can be purchased commercially or can be constructed using commercially-available instruments. The cost either way is relatively low. The commercial instruments can easily measure micro-coulomb amounts of charge, and, since the method whereby the oxide is reduced to a pre-defined reference state will involve a total charge of some coulombs, the measurement will be capable of very high sensitivity.

Regardless of which indirect method is used (solid state coulometric titration or thermogravimetry), a primary, direct method will also be required for establishment of the MO_2 reference state, determination of method bias, and periodic calibration. It was recommended that the following direct method be adapted for this purpose :

1. Oxygen measurement by inert gas fusion/carbon reduction, and total U,Pu by controlled potential coulometry.

Further, it is advisable that this direct method be used in conjunction with a certified reference standard material. This is particularly true in view of the uncertainties associated with the use of "thermodynamic standards" and the unproven equivalency of thermal treatments in the thermogravimetric method. It is probable that a series of Working Reference Materials (WRM) [16,17,18] will have to be fabricated. It is possible to fabricate such a WRM from either actual (U,Pu) mixed oxides or from a surrogate material.

Because of the possibility of "O/M drift" in a real oxide during prolonged storage, a surrogate oxide of $\text{Ti}_3\text{O}_5/\text{ThO}_2$ has been suggested,[19] where the titanium suboxide serves as the variable-stoichiometry phase and ThO_2 acts as an inert matrix material.

The establishment of a WRM using (U,Pu) mixed oxides would involve [20]

1. Standardization of the feedstock materials (purity of starting oxides, their elemental composition, etc.)
2. Standardization of the pellet fabrication process (binder type and concentration, sintering time and temperature, furnace atmospheres, etc.)
3. Identification of the properties to be certified (elemental composition, pellet density, pellet dimensions, etc)
4. Determination of the quantity of WRM to be generated.

In addition, if (U,Pu) mixed oxides are used, it should be noted that WRM's should be generated for several values of Pu/U ratio. The basis of such WRM's should be NIST or IAEA-traceable starting materials, i.e., Certified Reference Materials (CRM's),

[21] available from, for example, New Brunswick Laboratory. The establishment of a WRM can proceed by two routes, either (a) pellets produced by the fabricator can be sent to New Brunswick for certification, or (b) pellets produced by New Brunswick can be certified for use by the fabricator. Since the object of the Los Alamos MOX Project is to evaluate the use of excess weapons Pu, which will contain known impurities, and since the goal of the WRM's is to establish routine analytical methods by the fabricator, a parallel approach will probably serve best. Pure PuO_2 and UO_2 can be blended and sintered into pellets, and these would be returned to New Brunswick for analysis, to determine baseline values of the certified properties and statistics of the analytical methods. Simultaneously, pellets fabricated by LANL, using materials from the stockpile, will be fabricated into pellets. These would then be sent to New Brunswick for certification. A stock of such certified pellets could then be available to the fabrication facility for their analytical needs.

In some of the experimental studies covered in the O/M evaluation, such working standards have been fabricated starting from high-purity uranium and plutonium metals.[22] There is evidence, however, that a reference material made by mixing the pure component oxide powders, themselves produced by oxidation of the pure metals may behave differently than a sintered pellet (due to effects related to surface-to-volume ratio, etc.).[23,24] Further, if the reference pellet is sintered, there is no guarantee that the O/M of the reference will not change as a result of the thermal treatment.

Table 1. Experimental Values of Accuracy/Precision for O/M Methods.

Method	Accuracy/precision	Ref.
Thermogravimetry	Oxidation to U_3O_8 : ± 0.002 in O/M	[25]
	Oxidation to UO_2 : ± 0.002 in O/M	[26,27]
Gasometric/Gas equilibration	Precision for UO_{2+x} stated to be ± 0.003 in x	[28]
Inert gas fusion (for oxygen) + total metals (U + Pu) by controlled-potential coulometry	Relative standard deviation for $(U_{0.8}Pu_{0.2})O_2$ stated to be 0.2 % Precision of ± 0.005 in O/M for 1 g samples	[29]
Fluorination	Coefficient of variance < 2 % for Y_2O_3	[30]
Compound Addition	Precision of ± 0.0008 in x for UO_{2+x} .	[31]
	Standard deviation of ± 0.002 in x for U_3O_{8-x} samples.	[32]
EMF Cell	Precision of ± 0.002 in O/M for UO_{2+x}	[33]
Coulometric Titration	Precision of ± 0.0004 for UO_{2+x}	[34]
	Precision of ± 0.002 in O/M for mixed oxide samples containing up to 4% PuO_2	[35]
Spectrophotometry/Absorptimetry	Reproducibility of ± 0.0002 in O/U for UO_{2+x}	[36]
	Accuracy of 1% in Pu(VI)/ Pu(total) ratio for Pu-bearing solutions	[37]
Polarography	Precision of ± 0.001 in O/M for UO_{2+x} .	[38]
	For UO_{2+x} , error is ± 0.0005 in the vicinity of UO_2 and ± 0.005 near $UO_{2.25}$.	[39]
Phosphorimetry/ Laser-Induced Phosphorescence	Unknown	[40]
Potentiometric Titration (which ?) Amperometric Titration Spectrophotometric Titration	± 0.001 in O/M for UO_{2+x}	[41]
Thermal Conductivity/Diffusivity	Conductivity measured = f (O/M), but no analysis of O/M = f (conductivity)	—
Heat capacity/Specific Heat	Heat capacity measured = f (O/M), but no analysis of O/M = f (heat capacity)	—

Melting Point	Melting point = $f(O/M)$ for PuO_{2-x} ,	[42]
	Melting point = $f(O/M)$ for UO_{2+x}	[43]
	Liquidus, solidus temperatures = $f(O/M)$ for $(U_{1-y}Pu_y)O_{2-x}$ for $y = 0.8, 0.6$ and 0.4	[44]
Thermal Expansion/Dilatometry	Unknown	[45]
Absorptivity/Transmissivity	Changes in x as small as 0.0002 are claimed to be detectable.	[46]
Streak Test	Approximately ± 0.05 in x for UO_{2+x}	[47]
Nuclear Reaction Analysis	Used to verify O/M ratios in V_2O_5 films determined by Rutherford Backscattering	[48]
Neutron Activation Analysis	Precision of better than 1 % claimed for O/U in UO_{2+x} pellets	[49]
Nuclear Resonance Scattering	Standard deviation estimated to be ≈ 3.5 % for O/Ti in TiO_2 films	[50]
Rutherford Backscattering Spectrometry	RSD of 2.0 % for 22 spectra of O/Al in Al_2O_3 ($Al/O = 0.67 \pm 0.01$) RSD of 4.5 % for 30 spectra of O/V in V_2O_5 ($V/O = 0.4 \pm 0.02$)	[51,52]
Thermoelectric Power	Not given	[53,54]
Resistivity/Conductivity	Not given	[55]
Hall Effect	Not given	[56]
AES/EIL	Not given	[57,58]
XPS/ESCA	Not given	[59]
Ion Scattering Spectrometry	Experimental error of ± 0.1 in O/M for Air oxidized $(Fe,Cr)_2O_{3-x}$ -type films	[60]
XRF	1.95 ± 0.08 for O/Ti in TiO_2	[61]
XRD	Precision in O/M of ± 0.001 for a $(U_{1-y}Pu_y)O_{2-x}$ solid solution	[62]
Neutron Diffraction	Not given	[63]
X-Ray Absorption	Not given	[64]
Vapor Effusion	Not given	[65]

REFERENCES

1. "Management and Disposition of Excess Weapons Plutonium: Reactor-Related Options", National Academy of Sciences Panel on Reactor-Related Options for the Disposition of Excess Weapons Plutonium (NAS, Washington, D.C., 1995) p. 17.
2. W.L. Lyon, "The Measurement of Oxygen to Metal Ratio in Solid Solutions of Uranium and Plutonium Dioxides", USAEC (General Electric Company) Report GEAP-4271 (1963).
3. P.O. Perron, "Thermodynamics of Nonstoichiometric Uranium Dioxide", Atomic Energy of Canada, Limited (Chalk River) Report AECL-3072 (1968).
4. T.M. Florence, "A Review and Comparison of Methods for the Determination of Oxygen/Uranium Ratios in Uranium Oxides", Analytical Methods in the Nuclear Fuel Cycle (IAEA, Vienna, 1972) pp. 45-55.
5. G.C. Swanson, "Oxygen Potential of Uranium-Plutonium Oxide as Determined by Controlled-Atmosphere Thermogravimetry", USERDA (Los Alamos) Report LA-6083-T (1975).
6. C.S. MacDougall, M.E. Smith and G.R. Waterbury, "Determination of Oxygen in Refractory Oxides", *Anal. Chem.* 41 (1969) pp. 372-374.
7. G.R. Waterbury, G.B. Nelson, K.S. Bergstresser, and C.F. Metz, "Controlled-Potential Coulometric and Potentiometric Titrations of Uranium and Plutonium in Ceramic-Type Materials", USAEC (Los Alamos) Report LA-4537 (1970).
8. H.S. Rosenbaum, "Nuclear Laboratory Techniques for Materials Research", *Trans. Amer. Nucl. Soc.* 10 (1967) pp. 502.
9. J.E. Rein, R.K. Zeigler, G.R. Waterbury, W.E. McClung, P.R. Praetorius and W.L. Devlin, "Quality Assurance Programme for Surveillance of Fast Reactor Mixed Oxide Fuel Analytical Chemistry", Nuclear Fuel Quality Assurance (IAEA, Vienna, 1976) pp. 149-163. Also, USAEC (Los Alamos) Report LA-UR-76-828 (1976).
10. C.F. Metz and G.R. Waterbury, "The Analysis of Nuclear Fuels - A Review", Analytical Methods in the Nuclear Fuel Cycle (IAEA, Vienna, 1972) pp. 155-172.
11. C.F. Metz, J.W. Dahlby and G.R. Waterbury, "Measurement of the Oxygen to Heavy Metal Atom Ratio in Unirradiated Mixed-Oxide Fuels", Analytical Methods in the Nuclear Fuel Cycle (IAEA, Vienna, 1972) pp. 35-43.
12. J.R. Rein, R.K. Zeigler and C.F. Metz, "LMBR/FFTF Fuel Development Analytical Chemistry Program (Phase II)", USAEC (Los Alamos) Report LA-4407 (1970).
13. M.W. Urie, M.C. Burt and W.L. Devlin, "A Comparison of Thermogravimetric Methods Used to Determine Oxygen-to-Metal Ratios in Mixed-Oxide Fuels", USAEC (Hanford Engineering Development Laboratory) Report HEDL-TME-72-56 (1972).
14. K. Teske, H. Ullmann and D. Rettig, "Investigation of the Oxygen Activity of Oxide Fuels and Fuel-Fission Product System by Solid Electrolyte Techniques, Part I. Qualifications and Limitations of the Method", *J. Nucl. Mater.*, 116 (1983) pp. 260-266.
15. S.-H. Kang and H.I. Yoo, "Composition (x) Dependence of Nonstoichiometry (δ) in Ferrite Spinel $(\text{Mg}_x\text{Fe}_{1-x})_3\text{-}\delta\text{O}_4$ ", *J. Solid State Chem.* 139 (1998) pp. 128-134.
16. S.-T. Hsue, J.E. Stewart, T.E. Sampson, G. Butler, C.R. Rudy and P.M. Rinard, "Guide to Non-Destructive Assay Standards: Preparation Criteria, Availability, and Practical Considerations", USDOE (Los Alamos)

Report LA-13340-MS (1997).

17. "Standard Guide for Preparation of Working Reference Materials for Use in the Analysis of Nuclear Fuel Cycle Material", ASTM C1128-89 (ASTM, 1989).

18. J.E. Rein, G.L. Tietjen, R.K. Zeigler and G.R. Waterbury, "Preparation of Working Calibration and Test Materials: Mixed Oxide", USEAC (Los Alamos) Report LA-7322 (1978).

19. C.F. Hammond, R.E. Honnell and J.E. Rein, "Air-Stable Reference Material for Measurement of the Oxygen-to-Metal (O/M) Ratio of Nuclear Fuel", Proc. 26th Conf. Anal. Chem. Energy Tech. (Knoxville, TN, 1983) pp. 381-385.

20. P.M. Santoliquido, "Preparation and Certification of Uranium Oxide (U₃O₈) Spectrometric Reference Materials", J. Testing & Eval. 19 (1991) pp. 83-88.

21. S.P. Turel, "The Role of Certified Reference Materials in Material Control and Accounting", Nuclear Safeguards Technology 1978, vol. II (IAEA, Vienna, 1979) pp. 303-313.

22. I.R. McGowan, C.R. Johnson and K.A. Swinburn, "Oxygen/Metal Ratios in Plutonium/Uranium Oxide Fuels", Analytical Methods in the Nuclear Fuel Cycle (IAEA, Vienna, 1972) pp. 3-21

23. J.W. Dahlby, T.K. Marshall, G.R. Waterbury and G.C. Swanson, "Measurement of Oxygen-to-Metal Ratios in Uranium and Plutonium Oxides", USAEC (Los Alamos) Report LA-5329 (1973).

24. M.W. Urie, M.C. Burt and W.L. Delvin, "A Comparison of Thermogravimetric Methods Used to Determine Oxygen-to-Metal Ratios in Mixed Oxide Fuels", USAEC (Hanford Engineering Development Laboratory) Report HEDL-TME-72-56 (1972).

25. E.A. Schaefer and J.O. Hibbits, "Determination of Oxygen-to-Uranium Ratios in Hypo- and

Hyperstoichiometric Uranium Dioxide and Tungsten-Uranium Dioxide", Anal. Chem. 41 (1969) pp. 254-259.

26. G.C. Swanson, "Predictive Thermogravimetric Technique for Rapid Close-Coupled Oxygen-to-Metal Ratio Analysis of Uranium Plutonium Oxide", Proc. 21st Conf. Anal. Chem. Nucl. Fuel Reprocessing, (Science Press, Princeton, 1978) pp. 361-368.

27. R.E. Dahl, D.H. Nyman and J.M. Yatabe, "Remote Fabrication of Pellet Fuels for United States Breeder Reactors", Trans. Amer. Nucl. Soc. 32 (1979) pp. 226-227.

28. Guidebook on Quality Control of Water Reactor Fuel, IAEA Tech. Rep. Ser. No. 221 (IAEA, Vienna, 1983).

29. C.S. MacDougall, M.E. Smith and G.R. Waterbury, "Determination of Oxygen in Refractory Oxides", Anal. Chem. 41 (1969) pp. 372-374.

30. G. Goldberg, A.S. Meyer, Jr. and J.C. White, "Determination of Oxides in Fluoride Salts by High-Temperature Fluorination with Potassium Bromotetrafluoride", Anal. Chem. 32 (1960) pp. 314-317.

31. T. Fujino and H. Tagawa, "Determination of Oxygen in Ternary Uranium Oxides by a Gravimetric Alkaline Earth Addition Method", Anal. Chim. Acta 107 (1979) pp. 365-371. Also, T. Fujino, H. Tagawa, T. Adachi and H. Hashitani, "A Gravimetric Method for the Determination of Oxygen in Uranium Oxides and Ternary Uranium Oxides by Addition of Alkaline Earth Compounds", Anal. Chim. Acta 98 (1978) pp. 373-383.

32. T. Fujino, K. Ouchi and T. Yamashita, "An Improved Gravimetric Method for Determining Oxygen in Binary and Ternary Uranium Oxides by Addition of Alkali or Alkaline Earth Metal Nitrate", Anal. Chim. Acta 147 (1983) pp. 423-428.

33. Guidebook on Quality Control of Water Reactor Fuel, IAEA Technical

Reports Series No.221 (IAEA, Vienna, 1983).

34. Guidebook on Quality Control of Water Reactor Fuel, IAEA Technical Reports Series No. 221 (IAEA, Vienna, 1983).

35. N.E. Barring and G. Jonsson, "Controlled-Potential Coulometric Determination of the Oxygen-Metal Ratio in Mixed Uranium-Plutonium Oxides", *Anal. Chim. Acta*, 50 (1970) pp. 229-236.

36. S. Kihara, T. Adachi and H. Hanitani, "Spectrophotometric Determination of the O/U-Ratio of Non-Stoichiometric Uranium Oxide", *Fres. Z. Anal. Chem.* 303 (1980) p. 28.

37. W. Dams, R. Krause and K.-H. Nelges, "Determination of Plutonium Concentration and Plutonium Isotopic Composition in Mixed Oxide Fuels", *J. Nucl. Mater.* 153 (1988) pp. 86-90.

38. Guidebook on Quality Control of Water Reactor Fuel, IAEA Technical Reports Series No. 221 (IAEA, Vienna, 1983).

39. R.M. Burd and G.W. Goward, "The Polarographic Determination of Hexavalent Uranium in Uranium Oxides: The Determination of Oxygen Uranium Ratios", USAEC (Bettis Plant) Report WAPD-205 (1959).

40. ASTM Designation D5174-91, "Standard Test Method for Trace Uranium in Water by Pulsed-Laser Phosphorimetry" (ASTM, West Conshohocken, PA, 1998).

41. Guidebook on Quality Control of Water Reactor Fuel, IAEA Technical Reports Series No. 221 (IAEA, Vienna, 1983).

42. E.A. Aiken and S.K. Evans, "A Thermodynamic Data Program Involving Plutonia and Urania at High Temperatures. Quarterly Report No. 3", USAEC (General Electric) Report GEAP-5634 (1968). Also, E.A. Aiken and S.K. Evans, "A Thermodynamic Data Program Involving Plutonia and

Urania at High Temperatures. Quarterly Report No. 4", USAEC (General Electric) Report GEAP-5672 (1968).

43. R.E. Latta and R.E. Fryxell, "Determination of the Melting Point of UO_{2+x} ", *Trans. Amer. Nucl. Soc.* 8 (1965) pp. 375. Also, R.E. Latta and R.E. Fryxell, "Determination of the Solidus-Liquidus Temperatures in the UO_{2+x} System ($-0.5 \leq x \leq 0.20$)", *J. Nucl. Mater.* 35 (1970) pp. 195-210.

44. E.A. Aiken and S.K. Evans, "A Thermodynamic Data Program Involving Plutonia and Urania at High Temperatures. Quarterly Report No. 3", USAEC (General Electric) Report GEAP-5634 (1968). Also, E.A. Aiken and S.K. Evans, "A Thermodynamic Data Program Involving Plutonia and Urania at High Temperatures. Quarterly Report No. 4", USAEC (General Electric) Report GEAP-5672 (1968).

45. D.G. Martin, "The Thermal Expansion of Solid UO_2 and (U,Pu) Mixed Oxides - A Review and Recommendations", *J. Nucl. Mater.* 152 (1988) pp. 94-101.

46. T.R. Griffiths, H.V. St. Aubyn Hubbard, G.C. Allen and P.A. Tempest, "A New Method for the Determination of x in UO_{2+x} : Optical Absorption Spectroscopy Measurements", *J. Nucl. Mater.* 151 (1988) pp. 307-312.

47. J.A.L. Robertson, "Some Consequences of Excess Oxygen in UO_2 ", in Radiation Effects in Refractory Fuel Compounds, ASTM Spec. Tech. Pub. No. 306, (ASTM, Philadelphia, PA, 1961) pp. 3-15.

48. W.D. Mackintosh and H.H. Plattner, "The Anodic Oxidation of Vanadium: Transport Numbers of Metal and Oxygen and the Metal/Oxygen Ratio in the Oxide Films", *J. Electrochem. Soc.* 123 (1976) pp. 523-527.

49. L. Holland, E.L. Machado and C.E. Calado, "Measurement of the Oxygen Content of Uranium Oxide Fuel and Stainless Steel", *Trans. Amer. Nucl. Soc.* 21, supp.2 (1975) pp. 58-60.
50. B.K. Patnaik, C.V. Leite, G.B. Baptista, E.A. Schweikert, D.L. Cocke, L. Quinones and N. Magnussen, "Methodology And Application of the Nuclear-Resonance Reaction $^{16}\text{O}(\alpha, \alpha)^{16}\text{O}$ for the Profiling of Titanium-Oxide", *Nuclear Instruments & Methods B35* (1988) pp. 159-166.
51. H.J. Matzke and A. Turos, "Mechanisms and Kinetics of Leaching of UO_2 in Water", *Solid State Ionics* 49 (1991) pp. 189-194.
52. W.D. Mackintosh and H.H. Plattner, "The Anodic Oxidation of Vanadium: Transport Numbers of Metal and Oxygen and the Metal/Oxygen Ratio in the Oxide Films", *J. Electrochem. Soc.* 123 (1976) pp. 523-527.
53. S. Iida, "Electrical Properties of Non-Stoichiometric Uranium Dioxide", *Jap. J. Appl. Phys.* 4 (1965) pp. 833-838. Also, S. Iida, "Electrolysis and Ion Transport Mechanism in Uranium Dioxide", *Jap. J. Appl. Phys.* 6 (1967) pp. 77-82.
54. J.R. MacEwan, A. Harvey, M.J.F. Notley and H. Maki, "An In-Pile Study of the Thermal Conductivity and Electrical Properties of UO_2 and UO_{2-x} ", *Trans. Amer. Nucl. Soc.* 8 (1965) pp. 380-380. and
55. W.E. Bailey and W.L. Lyon, "Electrical-Property Study on UO_2 - PuO_2 Solid Solutions", *Trans. Amer. Nucl. Soc.* 8 (1965) pp. 34. Also, W.E. Baily and W.L. Lyon, "Some Electrical Properties of the Plutonium-Uranium Mixed Oxide System", USAEC (General Electric Company) Report GEAP-4675 (1965). Also, S.K. Evans and W.L. Lyon, "An Electrical Probe for Checking Homogeneity in Mixed-Oxide Fuel Pellets", *Trans. Amer. Nucl. Soc.* 10 (1967) pp. 99-100.
56. P. Nagels, M. Denayer and J. Devreese, "Electrical Properties of Single Crystals of Uranium Dioxide", *Solid State Comm.* 1 (1963) pp.35-40. Also, P. Nagels, J. Devreese and M. Denayer, "Electronic Conductivity in Single Crystals of Uranium Dioxide", *J. Appl. Phys.* 35 (1964) pp. 1175-1180. Also, J. Devreese, R. De Coninck and H. Pollak, "On the Conduction Mechanism in Uranium Dioxide", *Phys. Stat. Solidi* 17 (1966) pp. 825-829.
57. G.C. Allen and R.K. Wild, "Auger Spectroscopy of Uranium", *J. Chem. Soc., Dalton Trans.* (1974) pp. 493-498.
58. K. Winer, F. Wooten, C.A. Colmenares and R.L. Smith, "Luminescence of Thin Uranium Oxide Films", *J. Lumin.* 35 (1986) pp. 311-319. Also, K. Winer, C. Colmenares and F. Wooten, "Cathodoluminescence of Uranium Oxides", *J. Lumin.* 31&32 (1984) pp. 357-359.
59. S. Sunder and N.H. Miller, "Oxidation of CANDU Uranium Oxide Fuel by Air in Gamma Radiation at 150°C ", *J. Nucl. Mater.* 231 (1996) pp. 121-131. Also, S. Sunder, D.W. Shoesmith, M.G. Bailey and G.J. Wallace, "Mechanism of Oxidative Dissolution of Uranium Dioxide Under Waste Disposal Vault Conditions", *Proc. Intl. Conf. Radioactive Waste Management*, edited by M.A. Feraday (Can. Nucl. Soc., Toronto, 1982) pp. 398-405.
60. R.P. Frankenthal and D.L. Malm, "Analysis of the Air-Formed Oxide Film on a Series of Iron-Chromium Alloys by Ion-Scattering Spectrometry", *J. Electrochem. Soc.* 123 (1976) pp. 186-191.
61. V.R. Darashevich and B.A. Malyukov, "X-Ray Fluorescence and Gravimetric Determination of the Metal-to-Oxygen Ratio in Oxide Films", *Journal of Analytical Chemistry of the*

USSR (Zhurnal Analiticheskoi Khimii) 31 (1976) pp. 1174-1177.

62. R. Lorenzelli, R. Le Dudal, R. Atabeck, "Etude Hors-Pile des Reactions de UO_2 , PuO_2 et $(\text{U,Pu})\text{O}_2$ Avec le Cesium", Thermodynamics of Nuclear Materials (IAEA, Vienna, 1980) pp. 539-563.

63. S. Lizenga, A. Murasik, J. Leciejewicz and K. Solnicka, "On the Possibility of O/U Ratio Determination in UO_{2+x} Powder Samples by Neutron Diffraction", J. Nucl. Mater. 44 (1972) pp. 345-346.

64. L. Reiffel, "Measurement and Control Methods Using Radiation", Proc. 2nd United Nations Conf. Peaceful Uses Atomic Energy, vol. 19 (United Nations, Geneva, 1958) pp. 278-287.

65. G. Dean, J.C. Boivineau, P. Chereau and J.P. Marcon, "Contribution to the Study of the U-Pu-O System", Plutonium 1970 and Other Actinides, Nuclear Metallurgy, vol. 17 (TMS-AIME, New York, 1970) pp. 753-761.